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Corrosion Inhibition by Beet Root Extract

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Abstract

The inhibition efficiency (IE) of an aqueous extract of beet root (BR) in controlling corrosion of carbon steel in well water in the absence and presence of Zn^{2+} has been evaluated by mass loss method. The formulation consisting of 4 mL of BR extract and 50 ppm Zn^{2+} offers 98% inhibition efficiency to carbon steel immersed in well water. A synergistic effect exists between BR extract and Zn^{2+}. Addition of N-Cetyl-N,N,N – trimethylammonium bromide (CTAB) does not change the excellent inhibition efficiency of the BR – Zn^{2+} system. The BR – Zn^{2+} system shows excellent IE up to 7 days. Polarization study reveals that this formulation controls the cathodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} - betanin complex and $Zn(OH)_2$. The film is found to be UV - fluorescent.

***Keywords**:* carbon steel, corrosion inhibition, plant extract, beet root, beta vulgaris.

Introduction

Environmental friendly inhibitors have attracted several researchers. Natural products are nontoxic, biodegradable and readily available. They have been used widely as inhibitors. Natural products such as caffeine [1, 2] have been used as inhibitors. Corrosion inhibition of steel by plant extracts in acidic media has been reported [3, 4]. Scale inhibiting nature of plant extracts for various kinds of metals are summarized briefly [5]. Natural compounds as corrosion inhibitors for industrial cooling systems have been studied [6]. Aqueous extract of Rosemary leaves [7], Zenthoxylum - alatum [8] and Lawsonia [9] have been used to inhibit

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corrosion of metals. Corrosion inhibition of iron in hydrochloric acid solutions by naturally occurring Henna has been investigated [10]. An aqueous extract of plant material rhizome (Curcuma Longa L) powder has been used as a corrosion inhibitor for carbon steel [11]. Aqueous extracts of Onion [12], Andrograghis panizulata [13] have been used as corrosion inhibitors. Inhibitive action of Carcia papaya extracts on the corrosion of mild steel in acidic media and their adsorption characteristics have been studied [14]. Azadirachta indica in acid solution has good corrosion inhibitive property [15]. Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of Hibiscus rosa-sinensis Linn has been evaluated by mass-loss method and electrochemical studies [16]. Investigation of natural inhibitors is particularly interesting because they are non-expensive, ecologically friendly/ acceptable and possess no threat to the environment. The present work is undertaken:

(i) to evaluate the inhibition efficiency (IE) of an aqueous extract of beet root (BR) in controlling the corrosion of carbon steel in well water, in the absence and presence of Zn^{2+};

(ii) to examine the influence of N-cetyl - N,N,N-trimethylammonium bromide (CTAB), a biocide, and duration of immersion on the IE of the BR–Zn^{2+} system;

(iii) to analyze the protective film formed on the carbon steel by FTIR spectra and fluorescence spectra;

(iv) to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization studies and AC impedance analysis; and

(v) to propose a suitable mechanism for corrosion inhibition.

Experimental

Preparation of plant extract

An aqueous extract of beet root was prepared by grinding 10 g of beet root with double distilled water, filtering the suspending impurities, and making up to 100 mL. The extract was used as corrosion inhibitor in the present study.

Preparation of specimens

Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Mass-loss method

Relevant data on the well water used in this study are given in Table I. Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using Shimadzu balance, model AY 62. The corrosion products were cleansed with Clarke's solution [17]. The inhibition efficiency (I.E.) was then calculated using the equation

$$I.E = 100\,[1-(W_2/W_1)]\ \%$$

where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

Table 1. Parameters of well water.

Parameter	Value
pH	8.38
Conductivity	3110 μ mhos/cm
TDS	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

Surface examination

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic study.

FTIR spectra

FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

Fluorescence spectra

These spectra were recorded in a Hitachi F – 4500 fluorescence spectrophotometer.

Potentiodynamic polarization

Polarization studies were carried out in an H&CH electrochemical work station impedance analyzer model CHI 660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements

The instrument used for polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance, R_t, and the double layer capacitance, C_{dl}, were calculated.

Results and discussion

Analysis of results of mass loss method

The corrosion rate (CR) of carbon steel immersed in well water (whose composition is given in Table 1) in the absence and presence of inhibitor systems are given in Tables 2-4. The inhibition efficiencies (IE) are also given in these Tables.

It is seen from Table 2 that the aqueous extract of beet root (BR) is not a good inhibitor to carbon steel in well water. 2 mL of BR show only 42% IE. As concentration BR increases, IE slowly decreases. That is, at higher concentrations, BR accelerates corrosion. It favours dissolution of carbon steel in well water.

Table 2. Corrosion rate (CR) of carbon steel immersed in well water, in the absence and presence of inhibitors, and the inhibition efficiency (IE) obtained by mass loss method. Immersion period: one day; inhibitor: 10% aqueous extract of beet root (BR) + Zn^{2+}.

BR extract mL	Zn^{2+} 0 (ppm)		Zn^{2+} 25 (ppm)		Zn^{2+} 50 (ppm)	
	CR (mdd)	IE %	CR (mdd)	IE %	CR (mdd)	IE %
0	38.18	-	38.18	--	38.18	--
0	-	-	35.12	8	29.8	22
2	22.14	42	0.76	98	0.76	98
4	52.31	-37	1.52	96	0.77	98
6	57.27	-50	1.91	95	0.78	98
8	62.62	-64	3.83	90	0.76	98

Influence of Zn^{2+} on the inhibition efficiency of BR

The influence of Zn^{2+} on the IE of BR is given in Table 2. In the presence of Zn^{2+} (25 ppm, 50 ppm) excellent inhibitive property is shown by BR. A synergistic effect exists between BR and Zn^{2+}. For example, 4 mL of BR accelerate corrosion of carbon steel (IE = -37%); 50 ppm of Zn^{2+} have 22% IE. But their combination has 98%. This suggests that a synergistic effect exists between BR and Zn^{2+}.

Table 3. Influence of CTAB on IE of beet root extract (BR) (4 mL) – Zn^{2+} (50 ppm).

BR extract mL	Zn^{2+} ppm	CTAB ppm	CR mdd	IE %
0	0	0	38.18	--
4	50	0	0.78	98
4	50	50	0.77	98
4	50	100	0.76	98
4	50	150	0.78	98
4	50	200	0.77	98

Table 4. Influence of duration of immersion on IE of BR (4 mL) – Zn^{2+} (50 ppm).

Immersion period (days)	**1**	**3**	**5**	**7**
CR, mdd System: BR(0 mL) + Zn^{2+} (0ppm) + well water	38.18	19.1	17.8	16.1
CR, mdd System: well water + BR (4 mL) + Zn^{2+} (50 ppm)	0.76	0.38	0.36	0.81
IE (%)	98	98	98	95

Influence of N-cetyl N,N,N – trimethylammonium bromide (CTAB) on the inhibition efficiency of BR (4 mL) – Zn^{2+} (50 ppm) system

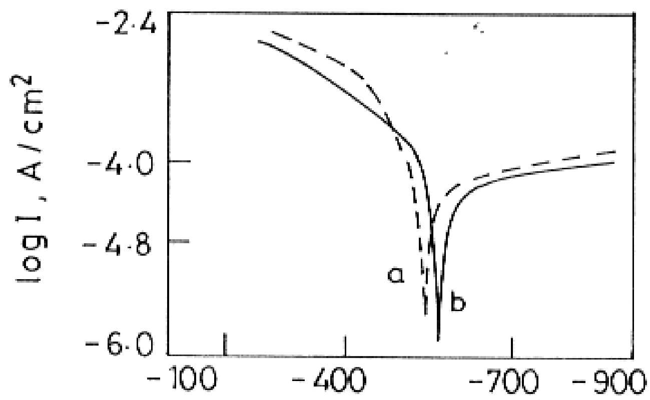
The influence of CTAB on the inhibition efficiency of BR (4 mL) –Zn^{2+} (50 ppm) system is given in Table 3. It is interesting to find that the IE of the BR – Zn^{2+} system is not changed by the addition of CTAB. CTAB is a biocide. It can control the corrosion caused by bacteria [18]. The present study reveals that the formulation consisting of BR, Zn^{2+} and CTAB has excellent corrosion inhibition efficiency. It is expected that this formulation will have excellent biocidal efficiency also. Hence this formulation may be used in cooling water system.

Influence of duration of immersion on the IE of BR (4 mL) – Zn^{2+} (50 ppm) system

The influence of duration of immersion on the IE of BR (4 mL) – Zn^{2+} (50 ppm) system is given in Table 4. It is found that the formulation consisting of BR and Zn^{2+} shows good IE even up to 7 days. The protective film is able to withstand the attack of the corrosive ions such as chloride ion (665 ppm) present in the well water.

Analysis of polarization curves

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 1. The corrosion parameters are given in Table 5. When carbon steel is immersed in well water the corrosion potential is -549 mV vs. SCE (Saturated Calomel Electrode). The corrosion current is 3.981 x 10^{-5} A/cm^2. When 4 mL of BR and 50 ppm of Zn^{2+} are added to the above system, the corrosion potential shifts to the cathodic side (-572 mV vs. SCE). This suggests that this formulation controls the cathodic reaction predominantly. In the presence of this inhibitor system, the corrosion current decreases from 3.981 x 10^{-5} A/cm^2 to 3.162 x 10^{-5} A/cm^2. This suggests the inhibitive nature of this inhibitor system.



E, mV vs. SCE

Figure 1. Polarization curves of carbon steel immersed in various solutions. a) Well water. b) Well water + 4 mL BR + 50 ppm of Zn^{2+}.

Table 5. Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitors. Inhibitor system: BR + Zn^{2+}.

BR mL	**Zn^{2+} ppm**	**E_{corr} mV vs. SCE**	**b_a mV**	**b_c mV**	**I_{corr} A/cm^2**
0	0	- 549	76	262	$3.981x10^{-5}$
4	50	- 572	119	71	$3.162x10^{-5}$

Analysis of AC impedance spectra

The AC impedance spectra of carbon steel immersed in well water, in the absence and presence of inhibitors are shown in Fig. 2. The AC impedance parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 6. When carbon steel is immersed in well water, the charge transfer resistance R_t is 60.06 ohm.cm^2; the double layer capacitance C_{dl} is $3.27x10^{-8}$ μ F/cm^2. When the formulation consisting of BR and Zn^{2+} is added, the R_t value increases and C_{dl} value decreases. This confirms that a protective film is formed on the metal surface. This decreases the corrosion rate of carbon steel and increases the inhibition efficiency.

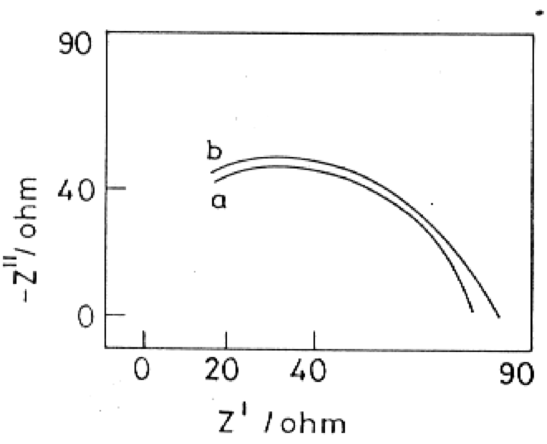


Figure 2. AC impedance spectra of carbon steel immersed in various solutions. a) Well water. b) Well water + 4 mL BR + 50 ppm of Zn^{2+}.

Table 6. AC impedance parameters of carbon steel immersed in well water in the absence and presence of inhibitors. Inhibitor system: BR + Zn^{2+}.

BR mL	**Zn^{2+} ppm**	**R_t Ohm.cm^2**	**C_{dl} μF/cm^2**
0	0	60.06	3.27x10^{-8}
4	50	68.22	2.88x10^{-8}

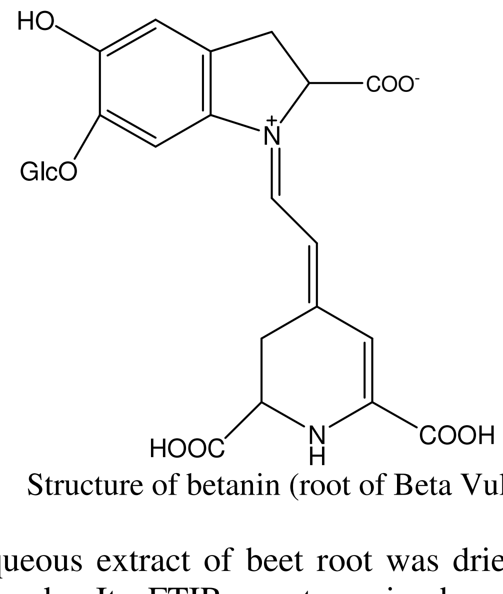
Comparison of results of mass loss method and electrochemical studies

In the present work mass loss study was carried out keeping the duration of immersion as 24 hours. It the electrochemical studies such as polarization and AC impedance, the instantaneous corrosion process is studied.

The mass loss study shows a tremendous difference between the corrosion rate of the blank system (well water only) and the inhibitor system (well water + BR 4 mL +Zn^{2+} 50 ppm); 98% IE is obtained. In polarization study the corrosion current is decreased only to a small extent (from 3.981x10^{-5} A/cm^2 to 3.162x10^{-5} A/cm^2). In AC impedance study the increase in R_t value (from 60.06 to 68.22 ohm.cm^2) and the decrease in C_{dl} value (3.27 x 10^{-8} to 2.88 x 10^{-8} μ F/cm^2) are very small. This is attributed to the various ions such as Ca^{2+} and Mg^{2+}, apart from chloride ion and sulphate ion. The various ions present in well water instantaneously form a protective film on the metal surface. But this film is broken in due course.

Analysis of FTIR spectra

The active principle in an aqueous extract of beet root is betanin. The red colour of the extract is due to betanin [19].



Structure of betanin (root of Beta Vulgaris)

A few drops of an aqueous extract of beet root was dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown Fig. 3a. The C=O stretching frequency appears at 1587 cm^{-1}. The OH stretching frequency appears at 3693 cm^{-1}. The C-N stretching frequency appears at 1248 cm^{-1}. The band due to conjugated double bonds appears at 3788 cm^{-1}. The asymmetric C-O-C stretching frequency appears at 1248 cm^{-1}. The symmetric C-O-C stretching frequency appears at 1068 cm^{-1}. Thus the structure of betanin is confirmed by FTIR spectra [20].

The FTIR spectrum of complex prepared by mixing BR extract and Fe^{2+} is shown in Fig 3b. The C=O stretching frequency shifts from 1587 cm^{-1} to 1595 cm^{-1}. The OH stretching frequency shifts from 3693 cm^{-1} to 3698 cm^{-1}. The C-N stretching frequency shifts from 1248 cm^{-1} to 1242 cm^{-1}. The band due to conjugated double bonds shifts from 3788 cm^{-1} to 3794 cm^{-1}. The asymmetric C-O-C stretching frequency shifts from 1248 cm^{-1} to 1242 cm^{-1}. The symmetric C-O-C stretching frequency shifts from 1068 cm^{-1} to 1097 cm^{-1}. These frequency shifts from BR show the formation of complex between BR and Fe^{2+} and betanin.

The FTIR spectrum of the film formed on the surface of the metal after immersion in the solution containing well water, 4 mL of BR and 50 ppm of Zn^{2+} is shown in Fig 3c. The C=O stretching frequency shifts from 1587 cm^{-1} to 1592 cm^{-1}. The OH stretching frequency shifts from 3693 cm^{-1} to 3697 cm^{-1}. The C-N stretching frequency shifts from 1248 cm^{-1} to 1255 cm^{-1}. The band due to conjugated double bond shifts from 3788 cm^{-1} to 3778 cm^{-1}. The asymmetric C-O-C stretching frequency shifts from 1248 cm^{-1} to 1255 cm^{-1}. The symmetric C-O-C stretching frequency shifts from 1068 cm^{-1} to 1066 cm^{-1}. These shifts confirm the formation of Fe^{2+} - betanin complex on the anodic sites of the metal surface. The peak at 1355 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface [21, 22].

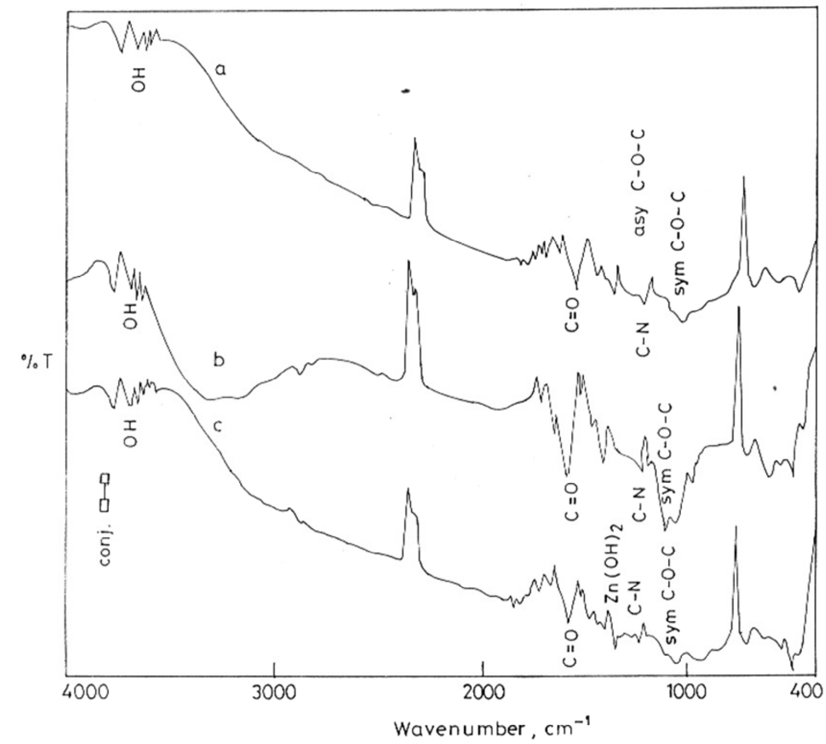


Figure 3. FTIR spectra. a) Solid mass obtained by evaporating the beet root extract (betanin). b) Fe^{2+} - betanin complex prepared. c) Film formed on surface of the carbon steel specimen after immersion in well water containing 4 mL of beet root extract and 50 ppm of Zn^{2+}.

Analysis of fluorescence spectra

A few drops of the BR extract were dried on a glass plate. A red solid mass was obtained. Its emission spectrum (λ_{ex}= 300 nm) is shown in Fig. 4a. Two prominent peaks appeared at 361 nm and 505 nm.

A few drops of the BR extract were mixed with a few drops of freshly prepared Fe^{2+} ions (ferrous sulphate). Fe^{2+} - Betanin complex was formed. It was dried. Its emission spectrum (λ_{ex}= 300 nm) is shown in Fig. 4b. The intensity of the peak at 361 nm decreased. The peak at 505 nm disappeared.

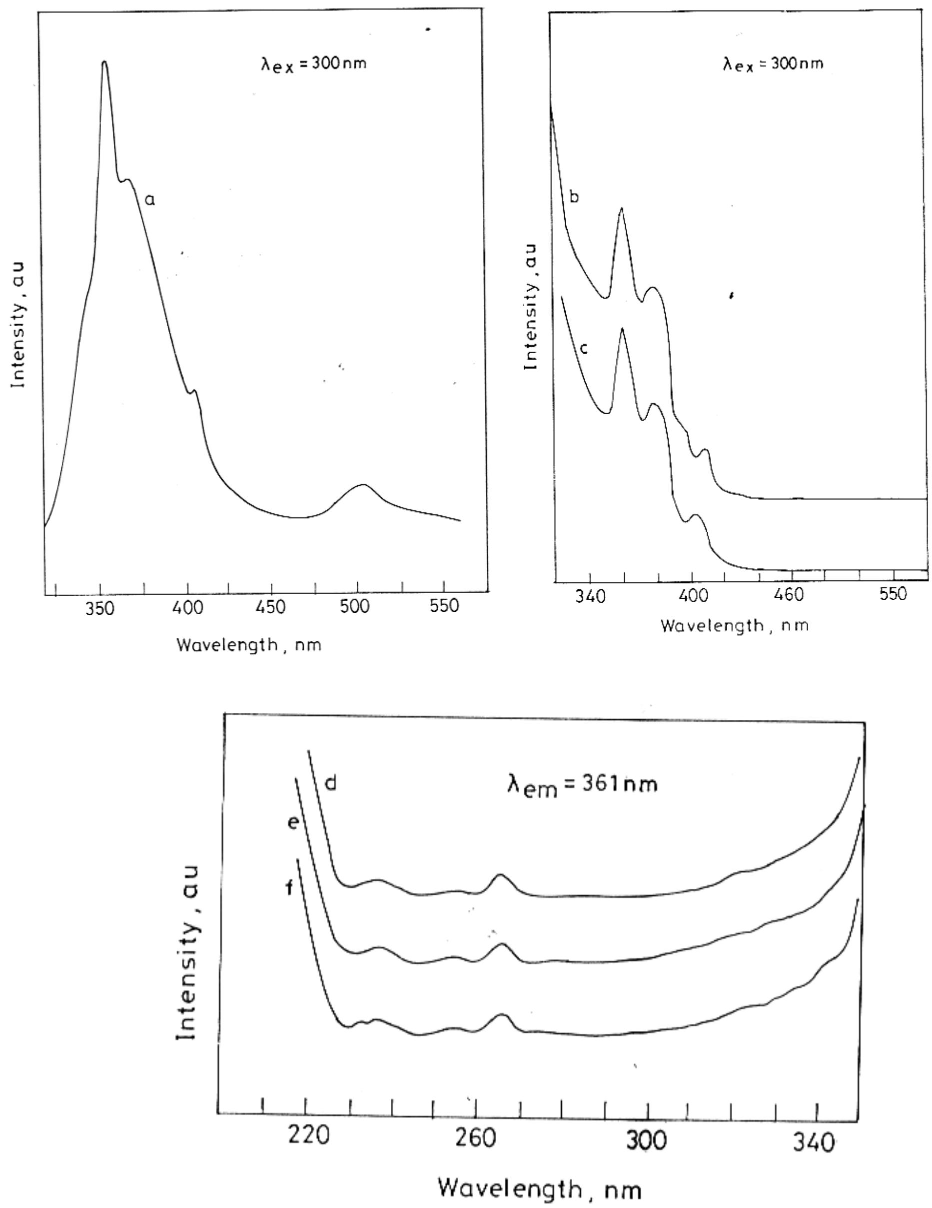


Figure 4. Fluorescence spectra. a) and (d): Emission and excitation spectra of solid mass obtained by evaporating beet root extract (betanin). b) and (e): Emission and excitation spectra of solid Fe^{2+} - betanin complex prepared. c) and (f): Emission and excitation spectra of film formed on surface of carbon steel specimen after immersion in well water containing 4 mL of beet root extract and 50 ppm of Zn^{2+}.

The emission spectrum (λ_{ex}= 300 nm) of the film formed on surface of the metal after immersion in the solution containing well water, 4 mL of BR and 550 ppm of Zn^{2+}, is shown in Fig. 4c. The nature of the spectrum matched well with that of the Fe^{2+} - betanin complex prepared. This confirmed the presence of Fe^{2+} - betanin complex formed on the anodic sites of the metal surface.

The excitation spectra (λ_{ex} = 361 nm) corresponding to Fig. 4a, b and c, are shown in Fig. 4d, e and f, respectively. A peak appeared at 265 nm, in all the cases.

Mechanism of corrosion inhibition

Mass loss study reveals that the formulation consisting of 4 mL of BR and 50 ppm of Zn^{2+} offers 98% IE to carbon steel immersed in well water. A synergistic effect exists between BR and Zn^{2+}. Polarization study reveals that this formulation controls the cathodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} - betanin complex and $Zn(OH)_2$.

In order to explain the above facts in a holistic way, the following mechanism of corrosion inhibition is proposed.

- When the formulation consisting of well water, beet root extract and Zn^{2+} is prepared, there is formation of Zn^{2+} - betanin complex in solution.
- When carbon steel is immersed in the solution, the Zn^{2+} - betanin complex diffuses from the bulk of the solution towards the metal surface.
- On the metal surface, Zn^{2+} - betanin complex is converted into Fe^{2+} - betanin complex. Zn^{2+} is released.

$$Zn^{2+} \text{ - betanin} + Fe^{2+} \rightarrow Fe^{2+} \text{ - betanin} + Zn^{2+}$$

- The released Zn^{2+} combines with OH to form $Zn(OH)_2$ on the cathodic sites.

$$Zn^{2+} + 2\ OH^{-} \rightarrow Zn(OH)_2 \downarrow$$

- Thus the protective film consists of Fe^{2+} - betanin complex and Zn $(OH)_2$. This accounts for the synergistic effect.

Conclusions

The present study leads to the following conclusions:

- the formulation consisting of 4 mL BR extract and 50 ppm of Zn^{2+} offers 98% inhibition efficiency to carbon steel immersed in well water;
- synergistic effect exists between BR extract and Zn^{2+};
- addition of N-cetyl – N,N,N, - trimethylammonium bromide (CTAB) (a biocide) does not change the excellent inhibition efficiency of the BR - Zn^{2+} system;
- BR – Zn^{2+} system shows excellent IE up to 7 days;
- Polarization study reveals that this formulation controls the cathodic reaction predominantly;
- AC impedance spectra reveal that a protective film is formed on the metal surface;
- FTIR spectra reveal that the protective film consists of Fe^{2+} - betanin complex and $Zn(OH)_2$;

- The film is found to be UV – fluorescent.

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